*Indian J. Phys.* **64B** (2), 152-159 (1990)

# Infrared and ultraviolet absorption spectra of some tri-substituted benzenes and their dipole moments in the first excited electronic states

M K Aralakkanavar, A M Joshi, Rekha Rao, K Suryanarayana Rao and M A Shashidhar

Department of Physics, Karnatak University, Dharwad-580 003, India

Received 11 July 1989, accepted 28 August 1989

The near ultraviolet and the vibrational spectra of aniline, benzonitrile, their mono and di derivatives have been studied in detail by different investigators (Green 1961, Green and Harrison 1979, Goel *et al* 1978, 1979, Goel and Agarwal 1982, Ginsberg *et al* 1946, Ginsberg and Matson 1947, Varsanyi 1974, Huded *et al* 1987, Shashidhar and Suryanarayana Rao 1966 and Evans 1960). As a part of our research programme and in continuation of our work on some aspects of the spectra of benzene derivatives, the present communication reports the study on the vibrational analyses of the infrared and UV absorption spectra of 3,4- and 3,5-difluoroanilines, 3-chloro-4-methyl benzonitrile and 3,5-difluorobenzonitrile (hereafter referred to as compounds I, II, III and IV). The solvatochromic shift of the $\pi^* \leftarrow \pi$ system of the compounds in different solvents have been utilised to calculate the electric dipole moments in the upper electronic states.

Compounds I and II are liquids while compounds III and IV are solids. They were obtained from Aldrich Chemical Co., USA and used to record the absorption spectra. The experimental methods adopted to record the i.r. and uv spectra and the accuracies in the measurement of band positions are the same as that given in our earlier work (Shashidhar 1971).

Compounds I and III may be considered as belonging to the point group $C_s$ while compounds II and IV may be considered as belonging to $C_{2v}$ point group if we consider the substituents to behave as a single mass point and coplanar with the ring.

The 36 and 42 normal modes of vibration for compounds I and III will have the distribution $25a' + 11a''$ and $29a' + 13a''$, all of these being active in i.r. spectrum. Under $C_{2v}$ symmetry of compounds II and IV, the 36 and 33 normal modes of vibration will have the distribution $13a_1 + 3a_2 + 12b_1 + 8b_2$

**Table I.** Correlation of the fundamental frequencies ($cm^{-1}$) of compounds I, II, III and IV.

| Compound I | | | Compound II | | | Compound III | | | Compound IV | | | Description of mode |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| IR | Electronic | | IR | Electronic | | IR | Electronic | | IR | Electronic | | |
| | GS | ES | | GS | ES | | GS | ES | | GS | ES | |
| 220 w | | | 220 mw | 225 ms | 88 s | 220 w | | | 225 m | | | X sensitive |
| 240 w | | | | | | 240 mw | | | — | | | $\gamma_{C-H}$ |
| 270 w | | | 260 mw | | | 260 w | | | 260 mw | | | X sensitive |
| 310 w | | | | | | 390 w | | | – | | | X sensitive |
| 390 s | — | 263 ms | 420 m | — | 375 s | 280 s | 282 w | 223 m | 450 m | — | 307 s | X sensitive |
| 405 ms | 405 mw | 311 s | 505 s | 505 m | 462 s | 460 s | 467 w | 421 m | 460 s | 453 m | 397 vs | X sensitive |
| 450 vs | 445 mw | 364 m | 330 s | 330 m | 232 s | 425 s | 425 w | 301 m | 330 w | 326 m | 223 ms | X sensitive |
| 470 w | 465 mw | 412 ms | 370 w | 366 mw | 270 s | 360 s | — | — | 420 s | 414 m | 359 s | X sensitiv |
| 520 m | | | 530 m | | | 605 w | | | 510 w | | | $\gamma_{C-C}$ |
| 605 s | 600 w | 452 s | 610 m | | | 605 vs | | | 600 ms | | | $^{9}C-C$ |
| 715 s | | | 730 ms | | | 700 s | | | 725 m | | | $\gamma_{C-C}$ |
| 735 vs | | | 806 s | | | 835 s | | | 870 vs | | | $\gamma_{C-C}$ |
| 770 vs | | 617 m | 670 s | 665 w | 552 s | 730 s | | 651 ms | 670 vs | | 510 s | X sensitive |
| 860 s | | 756 s | 1010 s | | 726 ms | 820 vs | | 738 m | 985 s | | 741 ms | X sensitive |

**Table I.** (Contd.)

| Compound I | | | Compound II | | | Compound III | | | Compound IV | | | Description of mode |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| IR | Electronic | | IR | Electronic | | IR | Electronic | | IR | Electronic | | |
| | GS | ES | | GS | ES | | GS | ES | | GS | ES | |
| 940 s | | | 805 s | | | 900 m | | | | | | $\gamma$C – H |
| 975 ms | | | 975 s | | | 920 m | | | 940 s | | | $\gamma$C – H |
| 1130 ms | | 914 m | 1120 s | | 834 ms | 1040 m | | 943 ms | 1050 m | | 968 s | $\beta$C – H |
| 1170 ms | | 1067 s | 1170 s | | 1043 m | 1150 w | | 1023 ms | 1140 s | | 1012 ms | $\beta$C – H |
| 1205 w | | 1166 ms | 1245 m | | 1128 m | 1210 m | | 1143 ms | 1260 s | | 1231 ms | X sensitive |
| 1245 vs | | 1191 ms | 1220 m | | 1193 m | 680 m | | 591 ms | 1230 s | | 1177 m | X sensitive |
| 1285 m | | | 1270 m | | | 1305 w | | | 1290 m | | | $\beta$C – H |
| 1315 vs | | 1247 m | 1300 ms | | 1235 m | 1190 s | | 1125 ms | 1160 m | | 1113 ms | X sensitive |
| 1340 w | | | 1330 ms | | | 1270 mw | | | 1325 ms | | | $\nu$C – C |
| 1430 vs | | | 1460 s | | | 1420 sh | | | 1420 s | | | $\nu$C – C |
| 1480 vs | | | 1380 s | | | 1480 sh | | | 1375 s | | | $\nu$C – C |
| 1570 m | | | 1570 m | | | 1590 m | | | 1590 vs | | | $\nu$C – C |
| 1600 m | | | 1605 s | | | 1540 m | | | 1610 m | | | $\nu$C – C |
| 3010 mw | | | 3080 w | | | 3020 sh | | | 3060 m | | | $\nu$C – H |

**Table I.** (Contd.)

| Compound I | | | Compound II | | | Compound III | | | Compound IV | | | Description of mode |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| IR | Electronic | | IR | Electronic | | IR | Electronic | | IR | Electronic | | |
| | GS | ES | | GS | ES | | GS | ES | | GS | ES | |
| 3040 sh | | | 3100 w | | | 3080 m | | | 3040 w | | | $\nu$C–H |
| 3080 ms | | | 3120 w | | | 3120 sh | | | 3080 s | | | $\nu$C–H |
| | | | | | | 570 m | | | 545 ms | | | $\beta$C=N |
| | | | | | | 2230 ms | | | 2230 s | | | $\nu$C=N |
| | Internal vibrations of $NH_2$ group | | | | | | | | Internal vibrations of $CH_3$ group | | | |
| 635 ms | | 620 m | | | $\gamma_{N-H}$ sym. | | | 870 s | | | $CH_3$ rock | |
| 1070 sh | | 1050 w | | | $\delta_{N-H}$ asym. | | | 1060 s | | | $CH_3$ rock | |
| 1620 m | | 1630 s | | | $\beta_{N-H}$ | | | 1380 s | | | C–H sym. def. in $CH_3$ group | |
| 3375 s | | 3360 ms | | | $\nu_{N-H}$ sym. | | | 1440 vs | | | C–H asym. def. in $CH_3$ group | |
| 3440 s | | 3430 s | | | $\nu_{N-H}$ asym. | | | 1460 vs | | | C–H asym. def in $CH_3$ group | |
| | | | | | | | | 2845 ms | | | C–H sym. stretch in $CH_3$ group | |
| | | | | | | | | 2920 s<br>2960 ms | | | C–H asym. stretch in $CH_3$ group | |

Letters in front of wavenumbers indicate the visual intensities of band observed.

mw = medium weak ; w = weak ; s = strong ; ms = medium strong ; vs = very strong ; m = medium ; sh = shoulder ; X = $NH_2$ in compounds I and II, $CH_3$ in Compound III and F in compound IV.

$\gamma$ = out-of-plane bend ; $\delta$ = in-plane bend ; $\nu$ = stretch ; sym = symmetric ; asym = asymmetric ; def = deformation.

**Table 2.** Static dielectric constant ($D$), refractive index ($n$) and spectral data ($\nu_{max}$ in $cm^{-1}$) for the solute molecules in different solvents used.

| Solvents used | Refractive index ($n$) | Dielectric constant ($D$) | $\nu_{max}$ (in $cm^{-1}$) | | | |
|---|---|---|---|---|---|---|
| | | | Compound I | Compound II | Compound III | Compound IV |
| Cyclohexane | 1.4260 | 2.0240 | 34190 | 36432 | 34906 | 35703 |
| Hexane | 1.3749 | 1.8836 | 34307 | 36486 | — | — |
| *n*-Heptane | 1.3870 | 1.9203 | — | 36480 | 35004 | — |
| Chloroform | 1.4460 | 4.8100 | — | 36221 | 34772 | — |
| Decalin | 1.4742 | 2.1530 | — | — | 34809 | — |
| Methanol | 1.3290 | 5.7210 | — | — | 35028 | 35262 |
| Iso-propylalcohol | 1.3770 | 20.3170 | 34050 | — | 34869 | 35450 |
| *n*-Propylalcohol | 1.3837 | 21.2400 | 340061 | 35909 | 34857 | 35387 |
| Carbon tetrachloride | 1.4595 | 2.2368 | 34096 | 36379 | 34809 | 35603 |
| Methylacetate | 1.3610 | 6.7210 | — | — | 35004 | — |
| Ethanol | 1.3600 | 3.4710 | 34260 | — | 34809 | — |
| Dichloromethane | 1.4240 | 9.0800 | — | 36169 | — | 35450 |
| Dimethylformamide | 1.4280 | 36.7100 | — | — | — | 35450 |
| *n*-Pentane | 1.3580 | 1.8371 | 34331 | 36512 | — | — |

and $12a_1+3a_2+11b_1+7b_2$ with all species active in i.r. spectra except $a_2$. The infrared absorption spectra of the compounds studied were analysed keeping in view the symmetry of the molecules, the analysed i.r. spectra of similar molecules. The fundamental vibrational frequencies along with thier assignments are given in Table 1.

The electronic absorption spectra of the compounds lie approximately in the region $\lambda$ 3090 to $\lambda$ 2550 Å and the bands are degraded to the red. The bands observed in this region corresponds to the forbidden electronic transition $^1B_{2u} \leftarrow {}^1A_{1g}$ of benzene. Under the reduced symmetry of $C_s$ or $C_{2v}$ of the compounds the above forbidden transitions become $^1A' \leftarrow {}^1A'$ in $C_s$ and $^1B_2 \leftarrow {}^1A_2$ in $C_{2v}$ and they are allowed.

The effect of temperature on the band system has facilitated the choice of the bands at 33258, 35624, 35334 and 35745 as the 0,0 band in compounds I, II, III and IV respectively. The identification of the fundamentals chosen in the compounds has been mainly done on the basis of the intensities of the bands and the available literature of other trisubstituted benzenes. The fundamentals so chosen are also listed in Table 1. The strong bands on the longer wavelength side with spacing 24 $cm^{-1}$ in compound I, 26 $cm^{-1}$ in compound II, 30 $cm^{-1}$ in compound III and 45 $cm^{-1}$ in compound IV have been indetified as sequence intervals.

**Table 3.** Values of electric dipole moments.

| Molecule | Ground state electric dipole moment $\mu_g$ in Debye units | Excited state electric dipole moment $\mu_e$ in Debye units | $\theta$ in degrees |
|---|---|---|---|
| Compound I | 4.05 | 5.87 | 53° |
| Compound II | 2.83 | 4.07 | 66° |
| Compound III | 3.75 | 6.18 | 58° |
| Compound IV | 2.54 | 5.35 | 78° |

The electric dipole moment of compounds I, II, III and IV in the first excited electronic state has been calculated using a new method given by Ayachit *et al* (1986) from the solvent effect on their electronic spectra. The $\nu_{max}$ values observed for $^1A' \leftarrow {}^1A'/{}^1B_2 \leftarrow {}^1A_1$ transition which are given in Table 2 are used to calculate $\mu_e$ and $\theta$, the direction of $\mu_e$. The values of refractive index ($n$) and dielectric constant (D) of solvents used are taken from literature (Weast 1973-74) and are also given in Table 2. The dipole moment in the ground state ($\mu_g$) has been calculated using the method of vectorial addition of group moments (Smallwood and Herzfeld 1930) and are given in Table 3. The molecular radius has been calculated using the method of atomic increments (Edward 1956).

The relevant plots obtained for the observed system of the compounds are given in Figures 1a, b, c and d. The values of $\mu_e$ and $\theta$ determined are given in

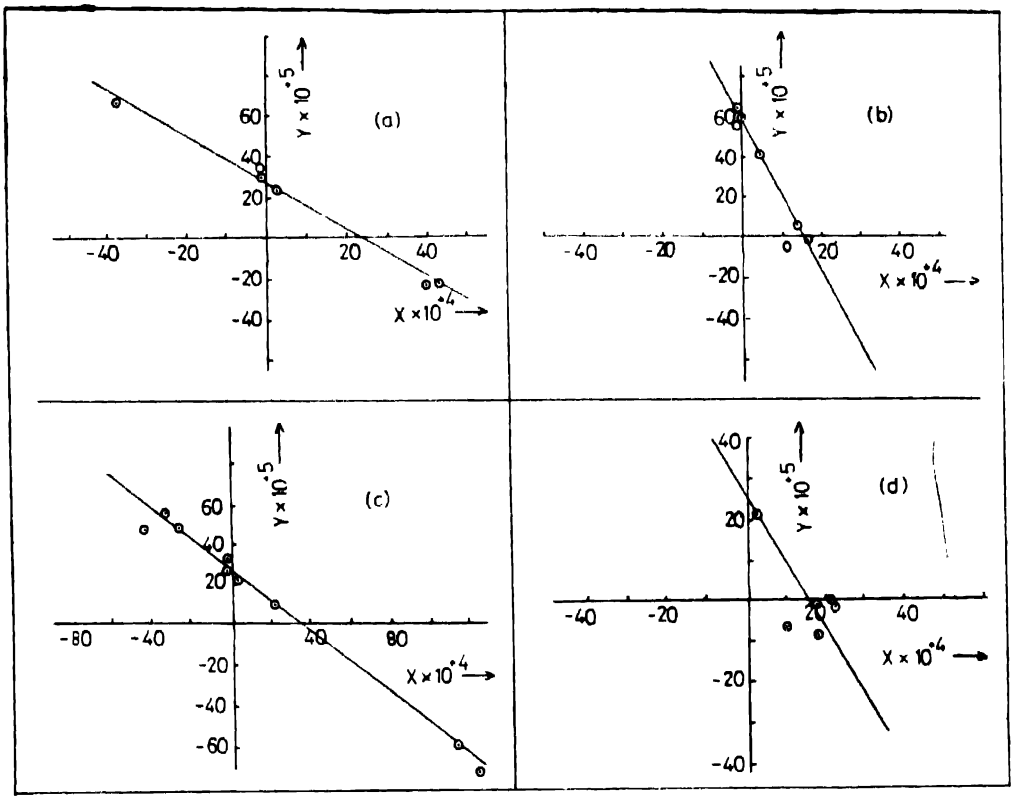


**Figure 1.** X vs Y plot for (a) compound I, (b) compound II, (c) compound III and (d) compound IV.

Table 3. It is expected that the values of $\mu_c$ should be greater for the upper state (Jaffe and Orchin 1962). In the present work this expected behaviour is observed.

## Acknowledgment

The authors (KSR and MAS) gratefully acknowledge with thanks the financial support by CSIR, New Delhi in the form of a research scheme.

### References

Ayachit N H, Deshpande D K, Shashidhar M A and Suryanarayana Rao K 1986 *Spectrochim. Acta* **42** 585

Edward J T 1956 *Chem. and Ind. (GB)*. 774

Evans J C 1960 *Spectrochim. Acta* **16** 428

Ginsberg N and Matson F A 1947 *J. Chem. Phys.* **13** 167

Ginsberg N, Robertson W N and Matson F A 1946 *J. Chem. Phys.* **14** 511

Goel R K and Agarwal M I 1982 *Spectrochim. Acta* **38A** 583

Goel R K, Gupta S K and Sharma S N 1978 *Pramana* **11** 541

Goel R K, Sharma S D and Sharma S N 1979 *Indian J. Pure Appl. Phys.* **17** 55

Green J H S 1961 *Spectrochim. Acta* **17** 607

Green J H S and Harrison D J 1979 *Spectrochim. Acta* **32A** 1279

Huded E V, Ayachit N H, Shashidhar M A and Suryanarayana Rao K 1987 *Indian J. Pure Appl. Phys.* **25** 289

Jaffe H H and Orchin M 1962 *Theory and Applications of ultraviolet spectroscopy* (New York : John Wiley)

Shashidhar M A 1971 *Spectrochim. Acta* **27A** 2363

Shashidhar M A and Suryanarayana Rao K 1966 *Indian J. Phys.* **40** 53

Smallwood H B and Herzfeld K F 1930 *J. Am. Chem. Soc.* **52** 1919

Varsanyi G 1974 *Assignments for vibrational spectra of seven hundred benzene derivatives* (London : Adam Hilger)

Weast R C 1973-74 *CRC Handbook of chemistry and physics 54th edn.* (Cleveland, USA : CRC Press)